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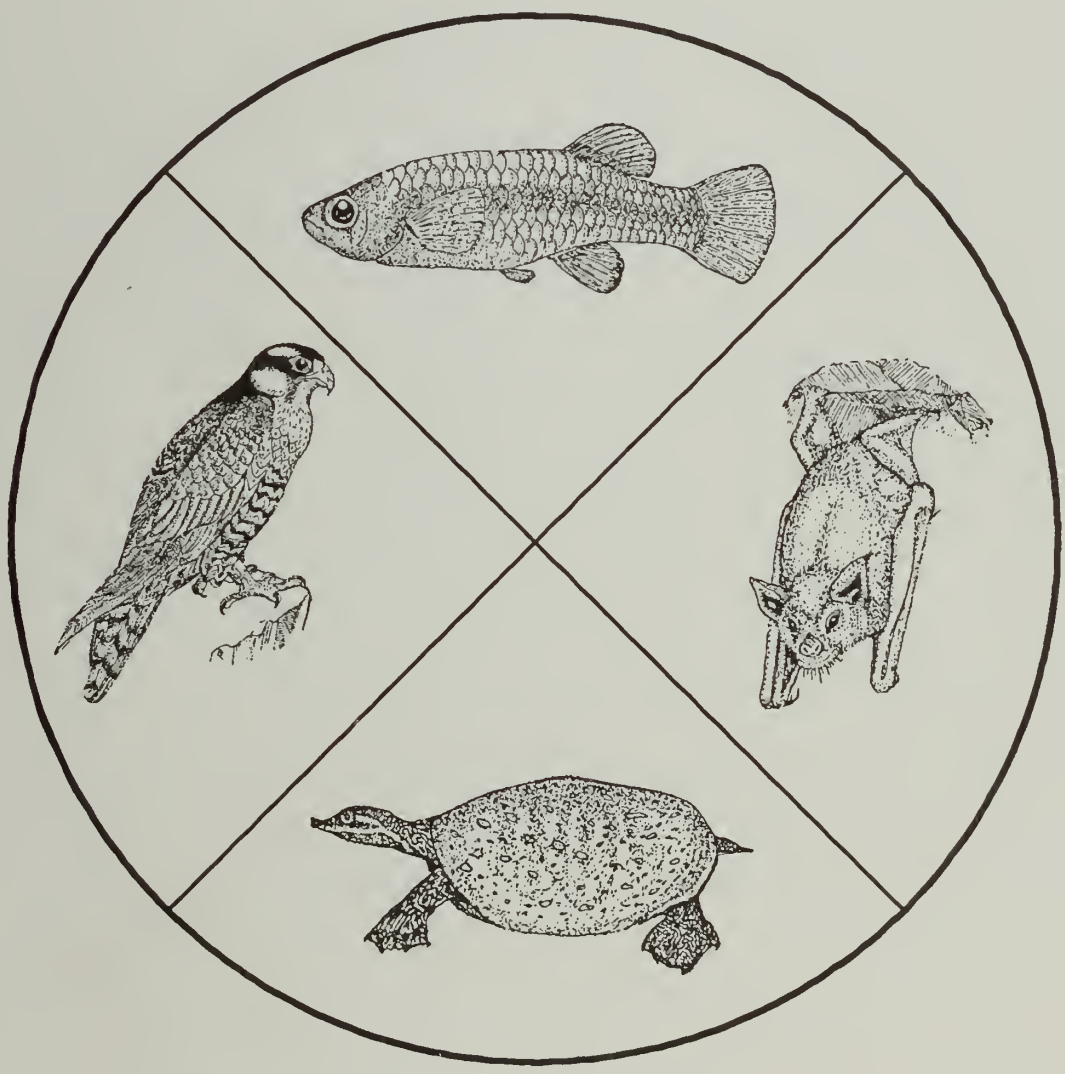
TOXIC CHEMICALS IN FISH AND WILDLIFE AT BIG BEND NATIONAL PARK, TEXAS



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TOXIC CHEMICALS IN FISH AND WILDLIFE AT BIG BEND NATIONAL PAP.K, TEXAS

ROY J. IRWIN
U.S. FISH AND WILDLIFE SERVICE
ECOLOGICAL SERVICES FIELD OFFICE
819 TAYLOR ST., ROOM 9A33
LANHAM FEDERAL BUILDING
FORT WORTH, TEXAS 76102

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EXECUTIVE SUMMARY/ABSTRACT

Residues of up to 67 chemical contaminants were measured in 53 samples of fish, turtles, insects, birds, and sediments from two Rio Grande sites. A total of 35 samples were analyzed for organochlorines and PCBs, 18 samples were analyzed for heavy metals, and 8 samples were analyzed for polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons. Except for DDT, DDD, and DDE, all samples were notably free of significant contamination by organochlorine contaminants. Mercury was only slightly elevated in most fish and wildlife samples and is not known to be an important cause of eggshell thinning in peregrines. Some of the levels of DDE, PAHs, and combined heavy metals in fish and wildlife tissues were sufficiently elevated to cause concern for predatory species of fish and wildlife.

DDE was found in concentrations exceeding predator concern levels in several small bird samples. DDE was also detected in a Rio Grande aquatic insect sample. Therefore, aquatic insects may be one source of DDE being biomagnified into the peregrine falcon food chain via insectivorous birds. In this way, the Rio Grande may be serving as one potentially harmful source of DDE available to the peregrine falcons in Big Bend National Park.

The Rio Conchos and other Mexican sources are suspected as the main source of DDE in the Rio Grande at Big Bend National Park. Continued sale of DDT in Mexico, its use in farming upstream in Mexico, and the presence of a pesticide facility upstream on the Rio Conchos (near Delicias, Mexico) have all been suggested as potential sources of DDT and its breakdown product, DDE, in the Rio Grande. More field investigations in Mexico in the Rio Conchos drainage upstream of its confluence with the Rio Grande would be necessary to more precisely identify the sources of DDE entering the Rio Grande from the Rio Conchos. Identifying and eliminating upstream sources of DDT/DDE and PAHs would probably be more helpful to the peregrine falcons and other fish and wildlife of the Big Bend area than carrying out additional field contaminant studies in the Rio Grande at Big Bend National Park at this time.

Keywords – Big Bend National Park Peregrine Falcons DDE Metals Residues Rio Grande Polycyclic Aromatic Hydrocarbons (PAHs)

INTRODUCTION

In recent years, peregrine falcon (Falco peregrinus anatum) populations in Big Bend National Park have been experiencing eggshell thinning problems and reduced hatching success has limited production of this endangered species [1]. DDE contamination has been suspected as a possible cause of these problems [1], partly because previous studies have indicated significant levels of DDE 100 miles upstream of Big Bend National Park (Jack Davis, Texas Water Commission, personal communication). However, data were lacking on the extent to which DDE might be accumulating in fish and wildlife in Big Bend National Park. Officials of the National Park Service asked the U.S. Fish and Wildlife Service to investigate this problem. Due to past hard rock mining activities in the area, Park Service officials also asked the U.S. Fish and Wildlife Service to determine whether or not selected species of fish and wildlife in Big Bend National Park were accumulating significant levels of mercury or other contaminants. With these issues in mind, the U.S. Fish and Wildlife Service initiated the first collections of small birds in Big Bend National Park in April, 1985. Collections of sediments, aquatic insects, fish, and turtles in the Rio Grande at Big Bend National Park were made during the spring of 1986.

There are over 62,000 chemicals that have been cataloged by the Environmental Protection Agency (EPA) in its Chemical Substances Inventory [2]. Due to cost and technology limitations, we analyzed 53 Rio Grande samples for 84 contaminants for comparison with levels of these chemicals in similar samples collected elsewhere. Only those contaminants meeting the following criteria were chosen for analysis: 1) chemicals that can routinely and reliably be quantified in fish and wildlife tissues by our contract laboratories, 2) persistent chemicals that are known to accumulate in specific categories of fish and wildlife tissues, and 3) chemicals, such as mercury, suspected to be present in Big Bend National Park due to past mining activities. Therefore, this study should be considered an initial exploratory survey, rather than a definitive follow-up study of all harmful chemicals that could possibly be accumulating in Big Bend National Park fish and wildlife.

MATERIALS AND METHODS

Sample Collections

Eight sediment and 37 tissue samples (listed in Appendix 1) were collected by the author from two Rio Grande sites (Figure 1). The site referred to as "Castolon" in the text and as "CAS" in Appendix 1 is a stretch of the river from Santa Elena Canyon to Castolon on the western side of Big Bend National Park. The site referred to as "Solis" in the text and "SOL" in Appendix 1 is a stretch of river from Solis to Casa de Piedra in the eastern part of the park. The Solis site is about 88 river kilometers downstream from Castolon and is just downstream of Mariscal Canyon. Like Santa Elena Canyon, Mariscal Canyon provides habitat for peregrine falcons.

Collections from Santa Elena Canyon to Castolon were made on April 17 and 18, 1986. Collections from Solis to Casa de Piedra were made on April 20 and 21, 1986. The river sections were floated with inflatable boats and stops were made to collect sediments and fish and wildlife at favorable locations along the way.

All collections of small fish were made with a 3.66 m minnow seine. Turtles and larger fish were collected with seines, gill nets, and hoop nets. The following species were collected at each site: mosquitofish (Gambusia affinis), Texas spiny softshell turtle (Trionyx spiniferus), channel catfish (Ictalurus punctatus), longnose gar (Lepisosteus osseus), and red shiner (Notropis lutrensis). Although we attempted to obtain gizzard shad (Dorosoma cepedianum) and river carpsucker (Carpriodes carpio) at both sites, we were successful in collecting these species only at Castolon.

Aquatic insect larvae (mostly dragonflies and hellgrammites) were collected at both sites with kick nets and seines. Adult flying insects (mostly dragonflies) were collected with sweep nets at Castolon.

Sediments were collected with a large, clean, stainless steel spoon. The samples were not sieved but only fines (the finest textured materials available) near the surface were collected. Each sample was a composite from several points while moving up and cross-stream. Banks and areas of sand or gravel were avoided. Samples for metallic analysis were placed in clean plastic bottles. Samples for organic analyses were placed in clean glass bottles with teflon liners. All sediment samples were kept frozen prior to laboratory analyses.

Eight samples of small birds were collected by shotgun from the same two sites. Danny Swepston of the Texas Parks and Wildlife Department, Alpine, Texas, collected these samples for us, using methods developed and approved

Fig. 1. Rio Grande collection sites in Big Bend National Park. Castolon site extended from Santa Elena Canyon Overlook to Castolon. Solis site extended from Solis to Casa de Piedra.

by the U.S. Fish and Wildlife Service. Northern rough-winged swallows (Stelgidopteryx serripennis), mourning doves (Zenaida macroura), cliff swallows (Hirundo pyrrhonota), and black phoebes (Sayornis nigricans) were collected at both Castolon and Solis on April 17, 1985.

On August 8 and 9, 1985, white-winged doves (Zenaida asiatica) and black phoebes were collected at both sites. Mourning doves were collected at Solis.

The birds were wrapped in aluminum foil and frozen, then sent directly to a U.S. Fish and Wildlife Service contract laboratory for analyses of organic contaminants (analyses for metallic contaminants were not requested for the bird samples).

Laboratory Methods

All chemical analyses were conducted at laboratories under contract to the U.S. Fish and Wildlife Service. Analyses were conducted for the 86 contaminants listed in Table 1, including 18 PAHs, 38 organochlorine compounds, 17 metallic contaminants, and 13 aliphatic hydrocarbons. All tissue concentrations are reported as mg/kg (parts per million) wet weight. Descriptions of samples, collection locations, and residue values for DDE, combined DDT, selenium, chromium, vanadium, mercury, percent (%) moisture, and percent (%) lipids are presented in Appendix 1 (aquatic samples) and Appendix 2 (bird samples).

All dissections were done by the author prior to shipment to the contract laboratories. Upon arrival at the contract laboratories, all tissue samples were chopped into small sections, composited, and ground to a fine homogenate.

A graphite furnace technique was utilized for aluminum, cadmium, lead, nickel, and chromium. Mercury was determined with a cold vapor atomic absorption spectrophotometer. A hydride generation atomic absorption spectrophotometer was used for arsenic and selenium, and all other metals were detected with an inductively coupled plasma atomic emission spectrophotometer (ICP).

Chemical analysis for organochlorines in tissues was accomplished by gas-liquid chromatography after extraction, gel permeation chromatography cleanup, and silica gel chromatography separation. Ten percent of the reported results were confirmed by gas chromatography-mass spectrometry.

Organic chemical analyses for birds were done at Mississippi State University and organic chemical analyses for the other samples were performed by Weyerhaeuser Analytical and Testing Services Laboratory of Federal Way, Washington. The Patuxent Wildlife Research Center in Laurel, Maryland performed the analyses for metals. These laboratories were subjected to a rigorous evaluation process prior to the award of their contracts. The Patuxent Analytical Control Facility of the U.S. Fish and Wildlife Service closely monitored the performance of these laboratories during the analyses and has confidence in the accuracy of the data. Acceptable performance (recovery variation <20% for all chemicals detected) on spikes, blanks, and duplicates was documented in laboratory quality control reports. However, the use of trade names for commercial laboratories is for identification purposes only and does not signify a recommendation by the U.S. Fish and Wildlife Service for the use of these laboratories for other purposes.

Statistical Methods

Statgraphics Version 2.6 from STSC, Inc. was the microcomputer software used for all statistical analyses. The differences between independent samples from the Rio Grande versus samples from the Trinity River were tested with the Mann-Whitney nonparametric statistical test. All references to "significantly lower" or "significantly higher" in this report refer to the level of statistical significance of $P<0.05$.

The statistical convention used to handle values below the detection limit was to transform them to a value half way between zero and the detection limit. This convention is recommended by U.S. Fish and Wildlife Service statisticians for studies such as this one, since a "non-detected" observation does not necessarily mean that the chemical was absent (Christine Bunck, U.S. Fish and Wildlife Service, personal communication). A non-detected observation signifies that the value is unknown and is somewhere between zero and the detection limit. Adopting this convention facilitates statistical analyses, and the use of low detection limits potential problems with the convention. However, text discussions of individual contaminants document detection limits and denote frequencies of instances with which the contaminant was below detection limits.

Table 1. Chemical Analyses, Rio Grande River, Texas, 1986.

ORGANIC CONTAMINANTS

Organochlorine scan:

Aldrin
Chlordane related:
- cis-Chlordane (alpha)
- trans-Chlordane (gamma)
- Oxychlordane
- cis-Nonachlor
- trans-Nonachlor
- Heptachlor Epoxide

Dacthal (DCPA)
DDT related:
- o, p'-DDE
- p, p'-DDE
- o, p'-DDD
- o, p'-DDT
- p, p'-DDD
- p, p'-DDT

Dicofol
Dieldrin
Endosulfan I
Endosulfan II
Endosulfan Sulfate
Endrin
Heptachlor
Hexachlorobenzene (HCB)
Hexachlorocyclohexane (BHC):
- alpha-BHC
- gamma-BHC (Lindane)
- beta-BHC
- delta-BHC

Methoxychlor
Mirex
PCBs:
- Arochlor 1016
- Arochlor 1221
- Arochlor 1232
- Arochlor 1242
- Arochlor 1248
- Arochlor 1254
- Arochlor 1260
- Arochlor 1262

Tetradifon
Toxaphene

Aliphatic Hydrocarbon Scan:

n-Dodecane
n-Eicosane
n-Heptadecane
n-Hexadecane
n-Nonadecane
Nonylcyclohexane
n-Pentadecane
Phytane
Pristane
n-Octadecane
Octylcyclohexane
n-Tetradecane
n-Tridecane

Polycyclic Aromatic Hydrocarbons (PAHs)

Acenaphthene
Acenaphthylene
Anthracene
1,2-Benzanthracene
Benzo(a)pyrene
Benzo(b)fluoranthrene
Benzo(e)pyrene
Benzo(g,h,i)perylene
Benzo (k) fluoranthrene
Chrysene
Dibenzo (a,h) anthracene
Fluoranthrene
Fluorene
Indeno (1,2,3-cd) pyrene
Naphthalene
Perylene
Phenanthrene
Pyrene

Table 1. continued

METALLIC CONTAMINANTS

Aluminum (Al)
Arsenic (As)
Beryllium (Be)
Cadmium (Cd)
Chromium (Cr)
Copper (Cu)
Iron (Fe)
Lead (Pb)
Magnesium (Mg)
Manganese (Mn)
Mercury (Hg)
Molybdenum (Mo)
Nickel (Ni)
Selenium (Se)
Tin (Sn)
Vanadium (V)
Zinc (Zn)

RESULTS

Low Level Contaminants

Aquatic Samples

Big Bend aquatic samples were notably free of elevated levels of many contaminants. The following organic contaminants were below laboratory detection limits in all aquatic samples (lowest wet-weight detection limits in mg/kg for tissues and sediments given in parentheses):

Aldrin (0.001)
BHC:
- alpha-BHC (0.003)
- gamma-BHC (Lindane) (0.003)
- beta-BHC (0.035)
- delta-BHC (0.006)

Chlordane related:
- cis (alpha) -Chlordane (0.002)
- trans (gamma) -Chlordane (0.002)
- Oxychlordane (0.002)
- cis-Nonachlor (0.003)
- trans-Nonachlor (0.002)
- Heptachlor Epoxide (0.002)

Dacthal (DCPA) (0.014)
o, p'-DDD (0.005)
o, p'-DDE (0.001)
Dicofol (0.003)
Dieldrin (0.003)
Endosulfan I (0.001)
Endosulfan II (0.001)
Endosulfan Sulfate (0.001)
Endrin (0.003)
Heptachlor (0.001)
Hexachlorobenzene (0.001)
Methoxychlor (0.004)
Mirex (0.002)
PCBs (0.011) (Arochlors 1016, 1221, 1232, 1242, 1248, 1254, 1260, and 1262)
Tetradifon (0.007)
Toxaphene (0.110)

The only metallic contaminant that was below laboratory detection levels in all samples analyzed for metals was beryllium, which had wet-weight detection limits of 0.10 mg/kg for tissues and 0.50 mg/kg for sediments.

Residues of several metals were in detectable ranges but not elevated compared to levels reported in national or regional studies [3,4,5,6,7,8,9]. Contaminants in this category included: aluminum, cadmium, iron, lead, manganese, molybdenum, tin, and zinc. Because such low levels of these chemicals were found in Big Bend samples, no separate text sections are provided for these contaminants.

Big Bend National Park's rural location tends to isolate it somewhat from many contaminants that are more common in urban environments. The levels of most contaminants (other than DDT/DDE) in Big Bend National Park aquatic samples were generally lower than those from similar samples in the Trinity River just downstream of Dallas/Fort Worth [4]. The Big Bend National Park samples also generally had lower concentrations of organic contaminants than similar samples collected from intense agriculture areas of the lower Rio Grande Valley [10]. Nevertheless, unexpectedly elevated concentrations of a few common urban contaminants were found in some of our Big Bend samples (see section on polycyclic aromatic hydrocarbons).

Bird Samples

Big Bend bird samples were analyzed for organochlorine compounds only. Except for DDE (p', p' DDE), these birds were notably free of elevated levels of organochlorines. The following organochlorines were below laboratory detection limits in all eight bird tissue samples (wet-weight detection limits were 0.01 mg/kg for all bird samples):

BHC:
- alpha-BHC
- gamma-BHC (Lindane)
- delta-BHC

Chlordane related:
- trans (gamma) -Chlordane
- cis (alpha) -Chlordane
- cis-Nonachlor
- trans-Nonachlor
- Heptachlor Epoxide

o, p'-DDE
o, p'-DDD
o, p'-DDT
p, p'-DDD
p, p'-DDT
Dieldrin
Endrin
Hexachlorobenzene
Total PCBs
Toxaphene

The following organochlorines were detected in at least one Big Bend bird sample but were not elevated in any sample above predator concern concentrations. The highest level found in Big Bend bird samples is given in parenthesis following the chemical name.

beta-BHC (0.05 mg/kg, rough-winged swallows from Castolon and Solis)
Oxychlordane (0.01 mg/kg, mourning doves from Castolon and Solis)
Mirex (0.03 mg/kg, cliff swallows from Castolon and Solis)

Concern and Comparison Levels

Accurately measuring concentrations of contaminants in fish and wildlife tissues is not a simple task. Many of the laboratories that our agency has tested as potential contract laboratories have been unable to pass our quality control checks and therefore have been disqualified from consideration. However, once an approved laboratory has correctly measured the concentration of a toxic chemical in a fish or wildlife tissue, it is usually still difficult to determine what this concentration means to the well-being of the organism or to predatory fish and wildlife species that might consume the organism. Detailed information on this subject is sparse.

There are no uniformly accepted standards for tolerable tissue concentrations of contaminants that will protect fish and wildlife and the predators that consume them. Instead, there is a hodgepodge of action and alert levels proposed by various agencies and experts for specific rather than uniform applications.

Some action or alert levels are based on fillet (edible to humans) samples, while others are based on whole-body samples. Some relate to fish only. For the contaminants that have been relatively extensively studied, like PCBs, there are many action or alert levels for comparison with our residue data. However, very few alert levels for fish and wildlife residues have been proposed for most of the contaminants detected in this study.

Given these facts, we have presented our results in contrast to as many action, alert, and comparison levels as we could identify. Our goal in doing this is to show the ranges of values for different types of samples and to shed as much light as possible on the meaning of our results. Since this initial exploratory survey utilized different species and tissue types, we have presented much of our data in the text rather than in tables in order to highlight the potential significance of elevated levels and to insure that comparisons utilize samples that are similar enough to be directly comparable.

Various species and tissue types are different in their efficiency at accumulating contaminants. For example, most organic contaminants tend to accumulate in fatty tissues, some metals tend to concentrate to higher levels in clams than in fish, and only a few contaminants have a tendency to concentrate in muscle (fillet) samples. Therefore, when comparing contamination levels at different sites, it is important not to directly compare whole-body contaminant concentrations with fillet (edible tissue) concentrations, nor to make comparisons involving two different species. However, when ranking different species and tissue types at a single station to determine which ones are the most efficient at bioaccumulating a given contaminant, all species and tissue types may be compared with each other. To facilitate both types of comparisons and help circumvent invalid comparisons, we have specified site locations, species, and tissue types in all text discussions of contaminant concentrations.

Five types of comparative levels for concentrations of contaminants in fish and wildlife tissues are mentioned in this report: Food and Drug Administration (FDA) action levels for human food, predator protection levels, predator alert levels, geometric mean levels from the National Contaminant Biomonitoring Program (NCBP), and gradient monitoring levels. Contaminants such as mercury have been extensively studied, so we have compared our results on mercury with all five types of concern or comparison levels. There are fewer (or no) concern or comparison levels for some other contaminants, so the text discussions of these contaminants are shorter and cover fewer comparisons. The five comparative levels are summarized as follows:

FDA Action Levels for Human Food are the standards utilized by the FDA for protection of human health in edible portions of fish and wildlife consumed by humans. Action levels for human food have been proposed for only a few of the contaminants listed in this report. In fish, action levels for human food relate to contaminant concentrations in fillets or muscle-only tissues rather than fatty tissues, bone tissues, or whole-body samples. Action levels represent limits at or above which FDA will take legal action to remove adulterated products from the market.

Our study was designed to primarily address impacts of contaminants on fish and wildlife rather than human health effects, so we analyzed few fillet samples of sportfish. Elevated contaminant levels in whole-body or fat-only samples of turtles or minnows do not necessarily equate to elevated levels in edible (fillet) tissues of sportfish. Since we took so few fillet samples and did not analyze our samples for every potential toxic chemical that could be present in fish tissues (see introduction section), no conclusions about human health effects of consuming fish from the Rio Grande should be drawn solely from our data.

Predator Protection Levels are the maximum concentrations recommended by various experts (designated in the text) for whole-body tissues of fish and wildlife prey species, to provide some measure of protection for the predatory species of fish and wildlife that are consuming them. Predator protection levels have been proposed for even fewer contaminants than FDA action levels. Unlike FDA action levels for human food, predator protection levels should be compared to whole-body contaminant concentrations.

Predator Alert Levels are levels of potential concern developed in this report based on derivations from human health standards or other rationale as stated in the text. Predator alert levels are provided for illustrative and discussion purposes rather than for regulatory purposes. The derivation of a predator alert level is meant to demonstrate the difficulty of developing "safe levels" and to illustrate why lower levels of contaminants may be necessary to protect fish and wildlife predators than to protect humans. Unless otherwise stated, predator alert levels refer to whole-body concentrations.

Mean NCBP Levels represent the geometric mean of whole-body concentrations of contaminants in fish, as reported in recent years by the National Contaminant Biomonitoring Program (NCBP) of the U.S. Fish and Wildlife Service [3,62]. Not all contaminants analyzed in this report are included in the NCBP. However, for some contaminants there are no action or alert levels and the NCBP mean is our only point of reference for comparison.

Gradient Monitoring Levels are used to measure the degree of contamination at various sites. As such, gradient monitoring levels are relative measures for comparison with each other rather than absolute measures for comparisons with action or alert levels.

Many of the gradient monitoring levels utilized in this report for comparison with Big Bend National Park levels are simply concentrations the author recently reported for the same species from the Trinity River in the Dallas/Fort Worth area [4]. The Trinity River provides a good "urban runoff" comparison to the relatively rural Rio Grande at Big Bend National Park. These comparisons were also interesting and convenient because: 1) many of the same species of fish and wildlife, especially mosquitofish and softshell turtles, were collected at both sites; 2) field and laboratory

methods were identical; and 3) both studies were conducted by the same person (the author) within a one year time-span.

The relatively small number of sites and sample replications that were used in this initial exploratory survey at Big Bend National Park do not lend themselves to extensive analyses of contaminant gradients at various sites along the Rio Grande. However, since we are comparing Rio Grande values to those derived from more extensive gradient monitoring analyses done at other locations, all such comparisons are discussed under subsections entitled "gradient monitoring levels." These are simply discussions of contaminants being higher or lower at one site than the other rather than concentrations exceeding concern levels.

Mosquitofish, the species used for gradient monitoring analyses, are not particularly effective accumulators of organic contaminants. Therefore, mosquitofish would not be apt to exceed action or alert levels for organics except at severely polluted sites. However, mosquitofish do accumulate at least low levels of most contaminants, when the contaminants are present in elevated amounts. One reason for using mosquitofish for gradient monitoring analyses was that they were present at all of our sampling sites on the Rio Grande and all of the comparison sites on the Trinity River [4].

Residue Levels

Aquatic Samples

p, p' DDE

DDE (p',p' DDE) is a degradation product of DDT, an insecticide that had widespread use before being banned in the U.S. in 1972 due to eggshell thinning and carcinogenicity concerns. DDE is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11]. Elevated levels of DDE in numerous wildlife species in New Mexico and Texas have been reported in several studies in the last 8 years [7]. In birds, migratory predatory species tend to accumulate the highest concentrations of DDE [12,13].

DDE was found above the detection limit (0.005 mg/kg) in 22 of 23 fish and wildlife tissue samples analyzed for organochlorines. DDE values for all samples are listed in Appendix 1.

Maximum Level: The highest value of DDE was 7.90 mg/kg in a composite sample of fatty tissue dissected from longnose gar collected at Castolon. Fatty tissue samples typically have much higher concentrations of fat (lipids) than whole-body or fillet samples, an important consideration since DDE tends to accumulate in fatty tissues. Thus, it is neither surprising nor conclusive that this gar sample was higher than the highest level (1.17 mg/kg) that has been reported from whole-body samples of longnose gar in the Trinity River [4]. The highest level of DDE found in birds was 4.9 mg/kg in a composite sample of 12 northern rough-winged swallows from Castolon and Solis (see Appendix 2).

Mean NCBP Levels: The national geometric mean of DDE for whole-body concentrations in fish is 0.20 mg/kg [3]. Whole-body fish samples of channel catfish, gizzard shad, river carpsucker, red shiners, and longnose gar from the Castolon area and channel catfish and longnose gar from the Solis area exceeded this level.

Gradient Monitoring Levels: In past years, spot checks of carp and various other fish species in the Rio Conchos and the Rio Grande at Presidio have revealed elevated levels of DDE (Charlie Sanchez, U.S. Fish and Wildlife Service, personal communication). However, since many of the fish we collected represent different species and species vary in their ability to concentrate DDE, we have included only comparisons of identical species. Directly comparable gradient monitoring data are summarized as follows:

Although we have some concern about DDE levels in Big Bend National Park due to the occurrence of peregrine falcons, the small amount of directly comparable anecdotal data available to us seems to indicate that DDE levels may be even higher upstream of Big Bend National Park in the area just downstream of the confluence of the Rio Conchos and far downstream in the lower Rio Grande Valley.

One whole-body sample of longnose gar collected (in 1979) just downstream of the confluence of the Rio Conchos by Texas Water Commission personnel, was found to have a DDE concentration of 5.9 mg/kg (Jack Davis, Texas Water Commission, personal communication). The whole-body sample of longnose gar we collected at Castolon in 1986 had a DDE concentration of 1.9 mg/kg (Appendix 1).

Also, just downstream of the confluence of the Rio Conchos, one whole-body composite sample of blue and channel catfish collected by the Texas Water Commission (on March 21, 1979, as part of the Presidio pesticide survey) was found to have a DDE concentration of 20 mg/kg (Jack Davis, Texas Water Commission, personal communication).

For contrast, the whole-body samples of channel catfish we collected from the Rio Grande in Big Bend National Park had DDE concentrations of 0.231 and 0.239 mg/kg (Appendix 1).

Fillet (edible tissue) samples of catfish showed the same trend. Just downstream of the confluence of the Rio Conchos, one composite sample of fillets from one blue catfish and one channel catfish collected by the Texas Water Commission on March 21, 1979, was found to have a DDE concentration of 18.68 mg/kg (Jack Davis, Texas Water Commission, personal communication). For contrast, the fillet samples of channel catfish we collected from the Rio Grande in Big Bend National Park had DDE concentrations of 0.126 and <0.097 mg/kg (Appendix 1).

A 1979 memorandum of the Texas Department of Water Resources (now Texas Water Commission) provided to us by its author, Jack Davis, also documents high concentrations of DDE in Rio Grande sediments just below the confluence with the Rio Conchos. Sediment concentrations near the mouth of the Rio Conchos ranged from 13 to 17.9 mg/kg DDE, while 37 kilometers downstream the concentration was 2.5 mg/kg. The sediment concentrations of DDE upstream of the Rio Conchos were below the 2.0 mg/kg detection limit. In findings similar to ours, the Texas Department of Water Resources also found that sediment concentrations in Big Bend National Park were below 2.0 mg/kg. One conclusion of the Texas Department of Water Resources memorandum was that Mexico, via inflow from the Rio Conchos, was the main contributor of DDT to the Rio Grande in the area of Presidio and just downstream.

Recent studies of fish and wildlife from the heavy agricultural areas in the lower Rio Grande Valley revealed slightly higher levels of DDE in sediments, fish, and softshell turtles than samples from upstream in Big Bend National Park or from the Trinity River [10]. The geometric mean for whole-body concentrations of DDE in softshell turtles from the lower Rio Grande was 2.38 mg/kg [10], a level considerably higher than the levels (0.05 to 0.08) we found in whole-body softshell turtle samples in Big Bend National Park.

Recent (unpublished) anecdotal data from the NCBP showed the same trend towards higher values of DDE in the heavily agricultural lower Rio Grande region than in the Rio Grande at Big Bend National Park. Concentrations of DDE in two whole-body samples of channel catfish collected in 1984 from the lower Rio Grande at Mission, Texas, as part of the NCBP were 1.55 and 1.21 mg/kg (Chris Schmitt, U.S. Fish and Wildlife Service NCBP Coordinator, Columbia, Missouri, personal communication). These lower Rio Grande concentrations were 5 to 6 times higher than the concentrations (0.21 and 0.22 mg/kg) we found in two whole-body samples of channel catfish from Big Bend National Park. Concentrations of DDE in two whole-body samples of gizzard shad collected in 1984 from the lower Rio Grande at Mission, Texas, as part of the NCBP were 1.27 and 1.44 mg/kg (Chris Schmitt, personal communication). As was the case for channel catfish, these lower Rio Grande concentrations are higher than the concentration (0.48 mg/kg) we found in a whole-body sample of gizzard shad from Big Bend National Park.

Concentrations of DDE in 4 samples of mosquitofish from the Rio Grande in Big Bend National Park were significantly higher than concentrations of DDE in 24 samples of mosquitofish from the Trinity River [4]. The elevation of whole-body concentrations in mosquitofish from Big Bend National Park compared to those from the Trinity River was more pronounced for DDE than for any other contaminant. None of the 24 Trinity River samples of mosquitofish exceeded 0.06 mg/kg DDE, whereas all 4 Big Bend samples exceeded that level.

Whole-body DDE levels in softshell turtles from Castolon ranged from 0.18 mg/kg (smaller turtles) to 0.53 mg/kg (larger turtles). These levels are higher than levels (0.05 and 0.08 mg/kg) found in whole-body samples of softshell turtles from relatively rural areas of the Trinity River [4]. By comparison, softshell turtles from a highly polluted storm drain site in downtown Fort Worth were somewhat higher (0.85 mg/kg) and values from a sample from a polluted site downstream of Dallas were in the same range [4].

In summary, the anecdotal gradient monitoring data we have seems to indicate somewhat elevated levels of DDE in aquatic biota of the Rio Grande in Big Bend National Park, although evidently not as highly elevated as levels just downstream of the Rio Conchos or far downstream in the lower Rio Grande Valley. However, the occurrence of peregrines in Big Bend National Park requires us to pay special attention to DDE levels that might be harmful to predators.

Predator Protection Levels: In general, it is difficult to determine truly "safe" levels for directive (relatively potent) contaminants such as DDT/DDE [65]. However, three bird samples (see Appendix 2) had concentrations of DDE higher than the 1.0 mg/kg predator protection level proposed by the National Academy of Sciences [17]. Although not elevated in comparison with the 1.0 mg/kg level, most Big Bend National Park aquatic samples generally had DDE levels higher than those found in similar samples from the Trinity River [4]. Since DDE is thought to be a major contributor to peregrine falcon declines in the Rio Grande drainage [7], the levels we are reporting here for birds,

aquatic insects, and other aquatic organisms may be cause for concern when bioconcentration factors are taken into account.

Typically, a large percentage of a red shiner's diet is aquatic insects [28]. The concentration of DDE in aquatic insects at Castolon was only 0.058 mg/kg, yet the concentration of DDE in whole-body samples of red shiners collected from the same site was 0.27 mg/kg. Thus, the preliminary indication is that predatory red shiners may be biomagnifying DDE to levels 5 times higher than those found in the aquatic insects. For comparison, one sample of red shiners from the Trinity River in Fort Worth had a concentration of 0.03 mg/kg DDE [4].

The fact that we found any DDE in the aquatic insect sample from Big Bend National Park may have significance for the predatory species of greatest immediate concern, peregrine falcons. The following factors are relevant: (1) the insect sample was fairly lean (5.9% lipids, thus we would not expect high levels of DDE); (2) some species of small birds can eat large quantities of emerging insects; (3) DDE has such a strong tendency to biomagnify (increase in concentration as it moves up the food chain); and (4) peregrine falcons consume considerable quantities of passerine birds that feed on insects. This issue is explored in more detail in the discussion section.

One sample of adult flying insects had less than 0.008 mg/kg DDE. However, we did not collect extensive samples of flying insects, and the particular insects we sampled (mostly large dragonflies) may not be the ones most important in the diet of insectivorous birds being eaten by the peregrines.

p, p' DDD

DDD was formerly marketed as the pesticide TDE. Like DDE, DDD is also a breakdown product of DDT. DDT is thought to be the main source of current residues of DDD. DDD is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11].

DDD was found above the detection limit (0.002 mg/kg) in 21 of 27 samples analyzed for organochlorines.

Maximum Level: The highest concentration of DDD was 0.51 mg/kg in a composite sample of fatty tissue dissected from longnose gar collected at Castolon.

Mean NCBP Levels: The national geometric mean of DDD for whole-body concentrations in fish is 0.07 mg/kg [3]. In our survey, none of the fish samples had whole-body concentrations of DDD above this level.

o, p'-DDT and p, p'-DDT

Residues of either o, p' DDT or p, p' DDT were above detection limits (0.007 mg/kg) in 5 of 27 samples analyzed for organochlorines.

Maximum Levels: The highest level of o, p' DDT was 0.014 mg/kg in eggs of longnose gar from the Solis site. The highest level of p, p' DDT was 0.26 mg/kg in the fatty tissues of longnose gar from the Castolon site. Whole-body samples of longnose gar and gizzard shad from the Castolon site, and channel catfish fillets from Solis, were the other three samples containing lower, yet detectable, levels of DDT.

Gradient Monitoring Levels: The levels of DDT found in Rio Grande samples are not high, but the fact that any detectable DDT was present is of interest. In 64 samples of fish and wildlife collected during 1985 from the Trinity River in north Texas, no DDT was detected [4].

No o,p' DDT was detected in a recent study of fish and wildlife from the heavily agricultural areas of the lower Rio Grande Valley far downstream of Big Bend National Park [10].

Combined DDT, DDE, and DDD

Combined DDT (totals of DDT, DDE, and DDD) detected in this study were not highly elevated compared to national surveys conducted in 1981 [3]. All combined DDT values are listed in Appendix 1.

Predator Protection Levels: Except for three samples of small birds (4.9, 2 , and 1.2 mg/kg) (Appendix 2), the only values above the 1.0 mg/kg recommended by the National Academy of Sciences for protection of predators from DDT residues in prey species [17] were from gar samples listed in Appendix 1 as samples 12 (8.67 mg/kg), 4 (1.9 mg/kg), and 20 (1.9 mg/kg). Although adult gar are relatively vulnerable to predation when spawning in shallow water, it is tough to eat an adult gar and they probably are not preyed upon much in the wild. Gar meat is sold for human consumption. In September of 1987, commercial fishermen were able to sell 18,000 pounds of gar meat from Sam Rayburn Lake in East Texas for 75 cents to $1.15 per pound [47].

However, the presence of DDE in aquatic insects provides one potential avenue for DDE to biomagnify up the avian food chain. Therefore, we conclude that the DDT and DDE brought in via the river may continue to pose a threat to peregrine falcons and other Big Bend predators.

Gradient Monitoring Levels: Combined DDT levels in 4 samples of mosquitofish from the Rio Grande in Big Bend National Park were significantly higher than the four Trinity River samples having the highest levels of combined DDT [4].

Combined DDT levels in softshell turtles showed a trend parallel to that recorded for DDE. Softshell turtles from Castolon were 0.195 mg/kg (smaller turtles) and 0.543 mg/kg (larger turtles). These levels are higher than levels (0.055 and 0.08 mg/kg) found in softshell turtles from relatively rural areas of the Trinity River [4]. By comparison, softshell turtles from a highly polluted storm drain site in downtown Fort Worth were somewhat higher (0.85 mg/kg), and a sample from a polluted site downstream of Dallas was in the same range [4].

Aliphatic Hydrocarbons

Aliphatic hydrocarbons are major components of motor oil and other petroleum products [38]. Like polycyclic aromatic hydrocarbons (PAH's), high aliphatic concentrations can be a clue that oil or petroleum pollution may be present, but some aliphatics also occur naturally [29, 30].

Aliphatics are also present in sewage [30], urban runoff [30], and municipal landfill leachates [50,51]. Some of these occurrences are probably the result of contamination of these mediums by petroleum products. Low levels of aliphatics also occur naturally [29, 30]. Aliphatics tend to be less toxic and carcinogenic than PAH's (Brian Cain, Fish and Wildlife Service, personal communication).

High levels of aliphatics were not suspected in Big Bend National Park. Due to cost, aliphatics were analyzed in only eight Rio Grande samples.

In a previous study of fish and wildlife tissues from an oil spill area in downtown Fort Worth, every aliphatic in the scan was detected above the 0.01 mg/kg detection limit [4].

Most Big Bend National Park samples contained little or no aliphatic contamination. The highest aliphatic levels were found in fatty tissues of longnose gar from the Castolon site, which contained detectable levels of only 6 of 13 aliphatics analyzed (Table 2). Longnose gar are predatory, long-lived, and contain significant amounts of fatty tissues. All of these factors help make gar relatively good accumulators of most organic contaminants.

Mosquitofish (samples 7 and 19, Table 2) from the Castolon and Solis sites had higher levels (0.25 and 0.12 mg/kg) of n-pentadecane than two samples (0.07 and 0.08 mg/kg) of mosquitofish from the Trinity River near Fort Worth [4]. The predominance of odd-numbered carbon chain n-alkanes over even-numbered carbon chains and the pristane to n-heptadecane ratio seem to indicate that the aliphatics from Big Bend may be from natural sources [29, 30]. However, we have little confidence in the validity of these ratios to identify sources of aliphatics in freshwaters of Texas, since they failed to correctly identify oil pollution as the source of aliphatics at active oil pollution sites we sampled on the Trinity and Pecos Rivers. All aliphatics detected in Rio Grande fish and wildlife are common components of used motor oil [38].

For comparison purposes, one sample of mosquitofish was collected from a west Texas site on the Pecos River at Iraan. This site has experienced recurrent oil pollution. In the Pecos River sample, the concentration of n-pentadecane was 0.06 mg/kg and the concentration of n-hexadecane was 0.22 mg/kg, levels very close to those found in the Big Bend National Park samples of mosquitofish (Table 2). The biological significance of these levels of aliphatics is unknown.

Polycyclic Aromatic Hydrocarbons (PAHs)

PAHs are sometimes referred to as polynuclear aromatic hydrocarbons or as polycyclic aromatic compounds. PAHs are also grouped in a category of chemicals referred to as aromatic hydrocarbons (AHs) in some publications.

Twelve of the 18 polycyclic aromatic hydrocarbons (PAHs) analyzed in this study have been listed by the EPA among 129 "priority pollutants" [11]. Five of them are also listed among the 25 hazardous substances thought to pose the most significant potential threat to human health at priority superfund sites [52].

Higher weight PAHs include some of the most carcinogenic chemicals known to man. Many PAHs, and several breakdown products of PAHs, have been documented to be tumorigenic, teratogenic, and mutagenic to a variety of fish and wildlife, including fish, birds, amphibians, and mammals [27].

Immunosuppressive effects have also been documented in mammals [31]. The otherwise hardy brown bullhead, Ictalurus nebulosus, is notably susceptible to PAHs, though evidence of cancer may not appear for 2 years after the initial exposure [53, 54].

Some plants can evidently catabolize benzo(a)pyrene, a PAH that some authors have referred to as the ultimate carcinogen, but metabolic pathways have not been clearly defined. When PAHs do degrade in plants through

Table 2

Residues of ALIPHATIC Hydrocarbons in MG/KG

Compound Name	Detection Limit	Sample 12	Sample 1	Sample 2	Sample 7	Sample 9	Sample 16	Sample 17	Sample 18
n-Dodecane	<0.05	ND	ND	ND	ND	ND	ND	ND	ND
n-Tridecane	<0.05	ND	ND	ND	ND	ND	ND	ND	ND
n-Tetradecane	<0.05	ND	ND	ND	ND	ND	ND	ND	ND
Octylcyclohexane	<0.05	ND	ND	ND	ND	ND	ND	ND	ND
n-pentadecane	<0.05	0.25	0.5	ND	0.25	ND	ND	ND	0.12
Nonylcyclohexane	<0.05	ND	ND	ND	ND	ND	ND	ND	ND
n-Hexadecane	<0.05	ND	ND	ND	ND	ND	ND	ND	ND
n-Heptadecane	<0.05	2.1 [c]	ND	ND	0.19	ND	0.06	0.08	ND
Pristane	<0.05	0.09	ND	ND	ND	ND	ND	ND	ND
n-Octadecane	<0.05	ND	ND	ND	ND	0.10	ND	ND	ND
Phytane	<0.05	0.10	ND	ND	ND	0.10	ND	ND	ND
n-Nonadecane	<0.05	0.60 [c]	ND	ND	ND	ND	ND	ND	ND
n-Eicosane	<0.05	0.10	ND	ND	ND	ND	ND	ND	ND

c - Confirmed by GC/MS

See Appendix 1 for Sample Descriptions

metabolism, they often break down into even more toxic, carcinogenic, and mutagenic compounds [27]. The PAH biomagnification potential of vegetation in terrestrial and aquatic food chains needs to be measured for a variety of PAHs in both field and laboratory experiments before we will have a complete understanding of these transformations [27].

Metabolic transformations of PAHs into even more hazardous chemicals could also occur in sediments, soils, and various species of fish and wildlife [27,36]. Metabolic degradation of carcinogenic PAHs proceeds very slowly in subsurface soil or sediment environments. This is because these environments are low in oxygen and sunlight [27].

Due to cost limitations, PAHs were analyzed in only 8 samples. Although PAHs can occur naturally in small concentrations, raw fish from unpolluted areas usually do not contain detectable concentrations of PAHs and highly elevated concentrations are usually the result of contamination from petroleum products or industrial activities [27]. PAHs usually make up 10 to 30% of crude oil and waste crankcase oil [38]. In rural areas, a considerable portion of PAHs in streams comes from highways [40]. Aquatic environments also receive PAHs from sewage treatment plants or atmospheric deposition [27].

Significant accumulation of PAHs in fish are of concern, since high quantities are very unusual; the carcinogenic PAHs usually are broken down quickly in the river [36]. Analyses of PAHs in fish tissues often show only traces of PAHs even when the sediments contain high concentrations of these compounds [36].

Maximum Levels: The highest PAH concentrations in our study were from composite whole-body samples of female mosquitofish from both Castolon and Solis. Both samples had higher levels of PAHs than we would have suspected from such a rural area.

The individual PAHs detected in these two mosquitofish samples (concentrations in parentheses as mg/kg, listed first for Castolon and second for Solis) included anthracene (0.28, 0.34); fluoranthene (0.08, <0.10); pyrene (2.1, 5.5*); 1, 2-benzanthracene (0.08, 0.16); chrysene (0.44, 0.68); benzo(k)fluoranthene (0.78, 0.98); benzo(e)pyrene (<0.14, 3.6*); perylene (0.30, <0.26); and indeno(1,2,3-cd) pyrene (0.20, <0.20). Most of these concentrations are lower than those reported to have caused a high incidence of liver cancer in bullhead catfish from a severely polluted river in Ohio [27]. However, some of these concentrations, especially those denoted with an asterisk, appear to be highly elevated compared to levels ($\leq$0.01 mg/kg) measured in mosquitofish from Mustang Creek and other relatively clean areas of the Trinity River [4].

Only two other Big Bend National Park samples had PAH values elevated above 1.0 mg/kg: 1.2 mg/kg of pyrene in fatty tissue of the longnose gar from Castolon and 1.6 mg/kg of indeno(1,2,3-cd) pyrene in one sediment sample from Solis.

Sediment Concern Levels: Wet-weight total PAHs in two sediment samples from Castolon were 0.645 and 0.75 mg/kg (0.42 and 0.52 total carcinogenic PAHs). Wet-weight total PAHs in two sediment samples from Solis were 3.04 and 1.6 mg/kg (2.06 and 1.6 mg/kg total carcinogenic PAHs). These levels are high enough to cause concern for bottom dwelling fish and wildlife.

Downstream of a creosote superfund site (Eagle Harbor site in Puget Sound), concentrations of total PAHs above 1.0 mg/kg dry weight had positive correlations with incidence of liver cancer in fish [37,41, confirmed by Don Malins, Pacific Northwest Research Foundation, personal communication]. A total PAH dry weight concentration of 1.0 mg/kg might typically correspond to a wet weight concentration of about 0.5 mg/kg and a total carcinogenic PAH level of 0.083 to 0.166 mg/kg.

If researchers at the Eagle Harbor site had used minimum detection limits for individual PAHs above 0.002 mg/kg, they would not have had the low level resolution to determine the 1.0 mg/kg total PAH level above which PAH concentrations were positively correlated with liver cancer in fish. This provides a convincing argument for the potency of PAHs and for using the lowest possible minimum detection limits at sites where one suspects PAHs as important contaminants.

Other researchers have also documented carcinogenic impacts from low levels of PAHs in sediments. For example, sediments from the Buffalo River, New York with concentrations of total carcinogenic PAHs as low as 1.0 mg/kg induced tumors in brown bullhead catfish [27].

Gradient Monitoring Levels: The two mosquitofish samples from Big Bend National Park previously mentioned as having the highest levels of PAHs were compared to similar samples from the Trinity River. These two samples had higher concentrations of PAHs than 12 of 13 mosquitofish samples collected in the Trinity River in the Dallas/Fort Worth area [4]. The only site on the Trinity River having higher levels of total PAHs was a highly polluted site just below Dallas, a site where greatly elevated levels of PAHs had previously been reported from sediments [4]. Levels of one

PAH, benzo(e)pyrene, in the Big Bend samples of mosquitofish were even higher than those from the highly polluted site below Dallas. The only Trinity River location having higher levels of anthracene, pyrene, 1, 2-benzanthracene, chrysene, and benzo(k)fluoranthene, than those recorded in Big Bend National Park was this same highly polluted site below Dallas [4].

The mosquitofish samples from Big Bend National Park had somewhat higher levels of total PAHs than those from two other significantly polluted Trinity River sites [4]. Levels of total PAHs were much higher in Big Bend samples of mosquitofish than they were in 6 samples from relatively unpolluted areas of the Trinity River [4].

The two Big Bend samples of mosquitofish were somewhat higher than a sample of mosquitofish collected in the spring of 1986 from a Pecos River site at Iraan that has experienced recurrent oil pollution (previously unpublished data collected by the author). The individual PAHs detected in the sample of mosquitofish from the Pecos River (concentrations in parentheses as mg/kg) included: anthracene (0.24); fluoranthene (0.54); pyrene (0.10); benzo(k)fluoranthene (0.56); and benzo(e)pyrene (0.48).

In Big Bend National Park, the levels of PAHs were somewhat higher at Solis but unexpectedly high for both locations, considering their rural setting. The sources of PAHs in Big Bend National Park are unknown. Fording of motor vehicles, disposal of used motor oil, or oil spills from upstream are all potential sources that warrant further investigation in the Big Bend area. Since the Rio Grande above the Rio Conchos confluence is often dry, the Rio Conchos drainage from Mexico may be a potential source of contaminants in the Rio Grande at Big Bend National Park (Jim Scudday, Sul Ross University, personal communication).

Arsenic

Arsenic is one of the few metals that tends to concentrate in axial muscles of fish [43]. However, clams are apparently more efficient arsenic accumulators than fish [5,11]. Arsenic is therefore of interest to those concerned with human health issues, since both fish fillets and clams are sometimes consumed by humans. Arsenic acts as a cumulative poison [25] and is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11]. A nationwide study of arsenic in bivalves showed less variation levels from various stations than was found for most other contaminants [46].

Arsenic enters rivers from air pollution (fossil fuel combustion) and soil erosion as well as from pesticides and industrial sources. Significant amounts of arsenic are known to leach from municipal landfills [55]. Pesticides are an additional source of arsenic in water [5].

Arsenic was found above the detection limit (0.05 mg/kg) in 14 of 18 tissue and sediment samples.

Maximum Levels: The highest concentration of arsenic in 4 sediment samples was 9.7 mg/kg in a sample from Solis (sample number 30 in Appendix 1). The highest concentration of arsenic in 14 tissue samples was 0.33 mg/kg in a whole-body sample of gizzard shad from Castolon (sample number 37).

Mean-NCBP Levels: The geometric mean of whole-body concentrations of fish in a 1978-1981 national survey was 0.14 mg/kg arsenic [62], a level exceeded in this study in only two whole-body fish samples: red shiners (0.26 mg/kg,sample 34) and gizzard shad (0.33 mg/kg,sample 37).

Gradient Monitoring Levels: The arsenic level in one composite sample of softshell turtles from Castolon was 0.17 mg/kg. This level is higher than those (0.025 to 0.060 mg/kg) found in softshell turtles from four sites on the upper Trinity River [4] and similar to levels found in the same species in the lower Rio Grande [10]. However, arsenic levels (0.07 to 0.14) in three samples of mosquitofish were not particularly elevated in relationship to mosquitofish samples from the Trinity River [4].

In the predominantly agricultural areas of the lower Rio Grande Valley (far downstream of Big Bend National Park) 14 of 32 fish had arsenic values exceeding 0.22 mg/kg (Larry Gamble, U.S. Fish and Wildlife Service, personal communication). However, different fish species and at least one brackish/marine species were analyzed for arsenic in the lower Rio Grande study, while all fish collected at Big Bend National Park were freshwater species. Therefore, the fish data for arsenic from these two Rio Grande sites are not directly comparable [10].

Predator Protection Level: Arsenic whole-body levels above 0.5 mg/kg are considered to be harmful to fish and predators [6]. None of our tissue samples exceeded this level. However, arsenic is one of those compounds for which more data are needed to assess precise risks to fish and wildlife and for which a zero level would be most effective at protecting from carcinogenic risk [66]. A zero level is probably currently not attainable, since arsenic enters rivers from air pollution (fossil fuel combustion) and soil erosion as well as from pesticides and industrial sources.

Chromium

Chromium is a metallic element that is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11], and is considered one of the 14 most noxious heavy metals [25].

Known sources of chromium include metal platers and a wide variety of chemical, photographic, power plant, and industrial facilities [75,68]. Soil, sediment, or mining sources may be playing a role in the elevated levels found in this study.

In the Solis area, natural weathering of volcanic rock between Castolon and Solis would be a potential source of elevated chromium levels (J.L. Whitford–Stark, Sul Ross University, personal communication).

Chromium concentrations above the detection limit (0.10 mg/kg) were found in 16 of 18 tissue and sediment samples analyzed for metals (Appendix 1).

Maximum Levels: The two highest concentrations of chromium in Big Bend samples were a composite sample of aquatic insects (2.4 mg/kg, sample 30) and a composite sample of softshell turtles (0.96 mg/kg, sample 35).

Predator Protection Level: Little is known about the effects of elevated tissue levels of chromium on fish and wildlife. Apparently, the only chromium level that has been proposed as a protective standard for animal tissues is 0.20 mg/kg [68]. Nine of the 14 tissue samples were above this level. In our recent study of fish and wildlife in the Trinity River, all tissue samples above 0.20 mg/kg were located downstream of urbanized Dallas/Fort Worth.

A survey of Pennsylvania fish from 16 sites revealed detectable chromium at 4 sites, with whole–body concentrations of chromium ranging from 0.1 to 0.26 mg/kg [5]. Based on our review of data from several U.S. Fish and Wildlife Service studies in the southwest, we consider chromium levels above 0.8 mg/kg in fish and wildlife tissues to be elevated [9,4,42]. That level was exceeded by 4 of 14 Rio Grande tissue samples.

Gradient Monitoring Levels: Twelve of 32 fish from the heavily agricultural areas of the lower Rio Grande Valley far downstream of Big Bend National Park had chromium values exceeding 0.20 mg/kg and 6 of 32 had values exceeding 0.8 mg/kg (Larry Gamble, U.S. Fish and Wildlife Service, personal communication). However, different fish species and at least one brackish/marine fish species were analyzed for chromium in the lower Rio Grande study, while all fish collected at Big Bend National Park were freshwater species. Therefore, the fish data for chromium from these two Rio Grande sites are not directly comparable [10].

Directly comparable data for these two sites is available for softshell turtles. The chromium level in one composite sample of softshell turtles from Castolon was 0.96 mg/kg. For contrast, the geometric mean of chromium concentrations in 22 softshell turtle samples from the Lower Rio Grande Valley was 0.34 mg/kg [10], and chromium concentrations in softshell turtles from four Trinity River sites ranged from 0.10 to 0.30 mg/kg [4].

Directly comparable fish data is available only from our recent Trinity River report [4]. The chromium levels (0.14 to 0.54 mg/kg) in 3 composite samples of mosquitofish from the Rio Grande were significantly lower than those found in mosquitofish from the upper Trinity River [4].

Copper

Copper is a commonly used metal and is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11].

Although copper is an essential dietary element for plants and animals, it can be toxic to fish [14]. Many researchers believe that negative effects of copper on fish would more likely be the result of toxicity of high concentrations in water than toxicity from intake of prey containing copper, but more data are required before the statement can be made with certainty [14] .

Copper is one of the most common contaminants associated with urban runoff, and specific sources include soil erosion, corrosion of pipes and tubes, industrial discharges, and sewage treatment plant discharges [14]. Copper acts synergistically with compounds of other common urban contaminants such as ammonia, cadmium, mercury, and zinc to produce an increased toxic effect on fish [15,48]. Sublethal concentrations adversely affect minnow fry survival and growth [5].

Copper concentrations above the detection limit (0.098 mg/kg) were found in 17 of 18 Rio Grande tissue and sediment samples. The only sample containing less than the detection level was a composite sample of aquatic insects from Castolon (sample 30).

Maximum Levels: The highest concentrations in Big Bend collections were from samples 44, 40, 32, and 33 (5.9, 2.6, 1.6, 1.5 mg/kg, respectively, see Appendix 1 for sample details). Four of the 5 highest concentrations were from mosquitofish.

Mean NCBP Levels: Copper whole-body levels above 0.9 mg/kg are higher than 85% of all fish in a NCBP national survey [62]. This level was exceeded in 9 of 14 Big Bend National Park tissue samples.

Gradient Monitoring Levels: The highest concentration of copper found in 32 fish samples from the heavy agricultural areas of the lower Rio Grande, far downstream of Big Bend National Park, was 5.09 mg/kg [10]. However, different fish species and at least one brackish/marine species were analyzed for copper in the lower Rio Grande study, while all fish collected at Big Bend National Park were freshwater species. Therefore, the fish data for copper from these two Rio Grande sites are not directly comparable [10].

In our recent study of the Trinity River, crayfish, turtles, and clams tended to be higher in copper than fish at identical sites [4]. A nationwide study of copper in bivalves showed less variation in levels from various locations than from various species [46].

The highest concentration (2.6 mg/kg) of copper from Rio Grande river mosquitofish was higher than was found in any of 24 mosquitofish samples from the urbanized upper Trinity River [4]. This finding is of interest because copper is one of the most common urban runoff contaminants and therefore might be expected to be more elevated in the highly urbanized parts of the upper Trinity than in rural areas.

Magnesium

Magnesium, a common component of the earth's crust, was detected in all samples. The only samples elevated above common levels found in fish (200–500 mg/kg) were both gar carcasses (samples 36 and 45). Little is known concerning whether or not highly elevated levels of magnesium in animal tissues might be harmful to the organism or fish and wildlife species which consume the organism. Magnesium has some useful physiological functions and small amounts of magnesium in the diet are therefore helpful to many organisms. Like calcium, small amounts of magnesium are often used as dietary supplements in multi-mineral pills consumed by humans.

Mercury

Mercury is a cumulative poison [25] and is the heavy metal most toxic to fish [16]. Mercury is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11].

Mercury is also one of the few metals that strongly bioconcentrates and biomagnifies [16]. Mercury has only harmful effects with no useful physiological functions when present in fish and wildlife [16]. Mercury is a carcinogen, mutagen, and teratogen [16]. Mercury is also easily transformed from a less toxic inorganic form to a more toxic organic form in fish and wildlife tissues [16]. It is a metal whose use should be curtailed as much as possible to prevent impacts to fish and wildlife [16]. When exposed to mercury in both mediums, fish accumulate more mercury from sediments than from water [56].

Current or past sources of mercury include batteries, vapor discharge lamps, thermometers, sewage treatment plant seals and discharges, the chloralkali industry, paints, pesticide compounds, switches, valves, dental labs and offices, mining, pharmaceuticals, laboratories, soil erosion, and air pollution deposition from fossil fuel combustion and smelters [16].

Mercury concentrations above the detection limit (0.05 mg/kg) were found in 11 of 18 samples of tissues and sediments (see Appendix 1 for all mercury values).

Maximum Levels: The highest value, 8.7 mg/kg, was from a composite sample of livers dissected from four longnose gar (sample 44). This value is higher than any other concentration we have found recorded in the literature for fish or wildlife tissues from any locality. Gar livers from sections of the Trinity River known to be polluted with mercury had mercury concentrations of 2.69, 1.02, and 1.31 mg/kg [49]. However, gar livers appear to be especially efficient accumulators of metallic contaminants [5,11]. The only other sample exceeding 0.5 mg/kg was also gar tissue (sample 36).

FDA Action Levels for Human Food and Other Human Health Standards: Human health standards for mercury in fish have included a 1.0 mg/kg U.S. FDA standard, a 0.5 mg/kg Canadian standard [19], and a 0.4 mg/kg Japanese standard [20]. The highest concentration of mercury in Big Bend National Park channel catfish fillet samples was 0.18 mg/kg (sample 41, a composite sample of fillets from the four largest catfish). Although this is above the predator protection concern level of 0.1 mg/kg (see following discussion), it is not particularly high in relationship to values found in other fish species in grocery store samples, and we generally expect larger fish to have higher levels. For perspective, the highest average market basket level reported by EPA for fish in 1980 was 0.27 mg/kg for yellow fin tuna [21] .

Predator Protection Level: A muscle tissue level of 0.232 mg/kg has been shown to cause decreased swimming in fish [5]. The most recently recommended level for the protection of avian predators that consume fish and other aquatic organisms is that total mercury in these food items should not exceed 0.1 mg/kg [16]. The author considers the 0.1 mg/kg alert level a bit high, if anything, since concentrations of 0.1 mg/kg fed to ducks produced reduced fertility and inhibited food conversion [21]. Other than the gar samples, the 0.1 mg/kg level was exceeded only in sample 41, a channel catfish fillet sample.

Predator Alert Level: Due to mercury's toxicity, an argument could be made for applying an application factor to FDA's 1.0 mg/kg action level for mercury. Assuming fish typically are eaten by humans at no more than 3 of 21 meals per week, and further assuming that fish usually account for no more than half of the food at each of those meals, a typical maximum percentage of fish in the human weekly diet could be estimated as 3 x 0.5 divided by 21 meals or 7.14% of the diet.

On the other hand, predators such as bass eat other fish and wildlife exclusively, and the tendency of contaminants like mercury to bioaccumulate in predators or biomagnify up the food chain make a lower standard necessary. Fish and wildlife predators usually consume the entire body of a prey species rather than fillets.

Concentrations of metal contaminants in muscle tissue are typically 0.5 to 0.6 of the concentration of a whole-body sample [26]. Dividing the 7.14% level by 2 to compensate for the difference between whole-body and muscle concentrations would yield a fish and wildlife application factor of 0.036. Multiplying 0.036 by the 1.0 FDA action level would yield a whole body alert level of 0.036 mg/kg, a level exceeded by 11 of 18 Rio Grande samples. The 0.036 mg/kg level is not much lower than concentrations fed to chickens (0.050 mg/kg) that resulted in chickens concentrating mercury to levels high enough to be of concern to human consumers [16] . However, more work would have to be done to definitively develop a predator alert level for mercury, so we have provided this simple derivation for illustrative and discussion purposes rather than for regulatory purposes.

Gradient Monitoring Levels: The mercury levels in 3 composite samples of mosquitofish from the Rio Grande at Big Bend were 0.025, 0.062, and 0.065 mg/kg. Only 5 of 24 upper Trinity River samples of mosquitofish exceeded 0.065 mg/kg, and all 5 were from sites downstream of Dallas [4].

The mercury level in one composite sample of softshell turtles from Castolon was 0.073 mg/kg. This level is somewhat higher than those (0.050 and 0.060 mg/kg) found in softshell turtles from two rural sites on the upper Trinity River [4]. However, it is lower than those (both 0.18) recorded for two highly polluted sites on the Trinity [4] and about the same as the geometric mean (0.062 mg/kg) of mercury concentrations in 26 softshell turtle samples from the lower Rio Grande Valley [10].

In Big Bend National Park, past mercury mining has resulted in high mercury levels in the soils of the Terlingua Creek area [39]. This area is upstream of our Castolon site. However, there was also past mercury mining in the Mariscal area, which is closer to the Solis site (J.L. Whitford-Stark, Sul Ross University, personal communication). We consider the levels of mercury found at both the Castolon and Solis sites to be only slightly elevated. Mercury in bottom sediments is resuspended during floods and carried further downstream. Such events have resulted in increased levels of mercury in fish, as noted in a previous U.S. Fish and Wildlife Service study in Montana [19].

Selenium

Like mercury, selenium tends to accumulate in the axial muscles of fish to a somewhat greater degree than some other metals [22,57], and muscle concentrations are typically 0.6 times whole-body concentrations [26]. Selenium also accumulates in the gonads of bass and bluegills [23] and has many teratogenic and toxic impacts upon fish and wildlife at high concentrations [24]. Selenium is one of 129 toxic pollutants listed by EPA as a "priority pollutant" [11].

Man's uses of selenium include photocopying, glass manufacturing, the production of stainless steel, fungicides, shampoos, lubricants, electronic devices, pigments, dyes, insecticides, and veterinary medicine [58,59]. Very high con-

centrations of selenium in fish and wildlife occur primarily in areas where selenium is naturally high in the soils or where coal fired power plants are present [24].

The range between insufficient selenium in the diet of animals and too much is narrow, and the effects of either problem can be serious [26]. Effects may range from birth defects to sterility and death [26].

Selenium was found above the detection limit in all samples (see Appendix 1 for selenium data).

Maximum Level: The highest value of selenium in tissues was 3.6 mg/kg, a level recorded for a composite sample of livers dissected from longnose gar (sample 44) .

Predator Protection and Mean NCBP Levels: Selenium whole-body levels above 0.5 mg/kg are considered harmful to fish and predators [6]. This concentration is close to the geometric mean of 0.47 mg/kg for whole-body concentrations of fish in a 1978-1981 national survey [62]. The 0.5 mg/kg level was exceeded in 7 of 14 Big Bend National Park tissue samples (Appendix 1) .

Gradient Monitoring Levels: The selenium level in one composite, whole-body sample of softshell turtles from Castolon was 0.64 mg/kg. This level is somewhat higher than those (0.26 to 0.43 mg/kg) recorded for similar softshell turtles samples from three sites on the upper Trinity River [4] and is also higher than the geometric mean selenium concentration (0.26 mg/kg) in 26 softshell turtle samples from the lower Rio Grande Valley [10]. However, it is about the same (0.67 mg/kg) as the concentration found in samples of the same species from a highly polluted Trinity River site just downstream of Dallas [4].

One whole-body sample of gizzard shad from Castolon had a selenium concentration of 1.1 mg/kg. This level is elevated compared to NCBP means [62], but is still somewhat less than the 2.42 mg/kg wet-weight concentration found in gizzard shad from Martin Lake in East Texas, the scene of selenium-related fish kills in 1978 and 1979 (Kirke King, U.S. Fish and Wildlife Service, Victoria, Texas, personal communication).

Two samples of mosquitofish from Castolon had concentrations of 0.45 mg/kg selenium. For contrast, mosquitofish from a severely contaminated pond at Kesterson National Wildlife Refuge in California had selenium concentrations ranging from 26 to 98 mg/kg [8,70].

A nationwide study of selenium in bivalves showed less variation in levels from various stations than was found for most other contaminants [46].

We were not able to locate information about selenium concentrations typical for soils in Big Bend National Park. However, the Rio Grande system upstream of Big Bend in New Mexico and Colorado runs through some areas where selenium is at least moderately elevated (Tom O'Brien, U.S. Fish and Wildlife Service, personal communication). Therefore, soil erosion may be a factor in selenium concentrations of aquatic biota in Big Bend National Park.

Vanadium

Vanadium is found in soil and is deposited in water as a result of fallout from air pollution [25]. Vanadium is considered to be one of the 14 most noxious heavy metals, but has a much higher bioconcentration potential in mollusks than in fish [25].

Vanadium was detected in 14 of 18 sediment and tissue samples (Appendix 1). Dietary vanadium has been shown to suppress egg production of laying hens [5]. Dietary vanadium at levels as low as 0.5 mg/kg has also been shown to alter metabolism in mallards [35]. This level was exceeded in 2 of our fish samples.

Gradient Monitoring Levels: Little comparative data are available for vanadium, but one composite sample of 5 softshell turtles from Castolon had a vanadium concentration of 0.20 mg/kg. This value is close to the 0.15 mg/kg geometric mean of vanadium concentrations recorded for 26 softshell turtle samples from the lower Rio Grande Valley [10].

Combined Heavy Metals

Studies of toxicity of contaminants on aquatic biota have suggested a wide range of responses of organisms to mixtures of toxic chemicals. Additive effects have been documented in various bioassay studies of aquatic organisms. Antagonistic effects (where toxicity is less for a combination of toxicants than for either toxicant alone) have also been reported. Synergistic (greater than additive) effects of lead and cadmium and additive effects of lead, mercury, copper, zinc, cadmiun, and mercury on aquatic biota have been documented for effects of metal concentrations in water [43].

Little information has been documented concerning the degree to which body burden combinations of these chemicals can cause greater effects on prey species and the predators consuming them than the effects of any single

contaminant. Fish and wildlife from polluted areas typically carry body burdens of several different toxic chemicals. Either additive or synergistic responses would result in cumulative impacts.

Metallothionein proteins can sequester and detoxify body burdens of cadmium, copper, mercury, and zinc only until a saturation level is reached [44]. According to the "spillover" theory, further additions of metal ions spill over into cellular components and cause pathological damage [44]. In riverine habitats, cumulative stress of combinations of toxic contaminants can suddenly result in very rapid degradation once a certain threshold (the system's assimilative capacity) is reached [45].

Predator Alert Level: A level of 0.5 mg/kg has been suggested as a high level at which arsenic, cadmium, lead, mercury, or selenium would harm fish [6]. To get an initial measure of combined heavy metals that are individually known to be harmful to fish and wildlife, we added the concentrations of the metals present in the Rio Grande that are thought to impact predators. Our combined heavy metals measure was obtained by adding concentrations of selenium, mercury, vanadium, arsenic, cadmium,and lead. Insufficient information is available to conclude whether or not 0.5 mg/kg is a harmful level for these combined heavy metals or to definitively develop a predator alert level for combined heavy metals, so we are comparing our concentrations with 0.5 mg/kg for discussion purposes rather than for regulatory purposes.

All 14 tissue samples (see Appendix 1 for a list of samples analyzed for metals) were above 0.5 mg/kg in combined heavy metals. If vanadium was excluded, only one sample (channel catfish fillet, sample 31) was below 0.5 mg/kg for combined heavy metals.

In a recent study of tissues of fish and wildlife from the Trinity River, only mosquitofish from relatively clean creeks were below 0.5 mg/kg for an identical measure of combined heavy metals [4]. However, we expected to find high levels of metals in the highly polluted Trinity. The Trinity samples were generally higher in urban contaminants such as cadmium and lead, but the Big Bend samples had notable elevations of selenium, chromium, arsenic, and vanadium. In a rural area like Big Bend National Park, mine sites and soil erosion are among possible sources of elevated metals.

Maximum Levels: Values of combined heavy metals above 1.0 mg/kg included gar livers (14.93 mg/kg, sample 44), gar carcasses (1.79 and 1.24 mg/kg, samples 36 and 45), softshell turtles (1.36 mg/kg, sample 35), gizzard shad (2.5 mg/kg, sample 37), mosquitofish (1.25 mg/kg, sample 40), and red shiners (1.63 mg/kg, sample 34). Some of these same samples also had elevated levels of DDE, but the combined effects of combinations of heavy metals and organic contaminants on predatory species of fish and wildlife are unknown.

Bird Samples

The eight bird samples collected in Big Bend were analyzed for organochlorine chemicals only. Except for DDE, levels of organochlorines were low in these samples (see section on low level contaminants).

p, p' DDE

Seven of eight bird samples had DDE concentrations exceeding the 0.01 mg/kg detection limit (Appendix 2). One mourning dove sample contained <0.01 mg/kg DDE. Since mourning doves are not predatory, it is not surprising that they should be carrying relatively low body burdens of DDE. Mourning doves eat plant seeds rather than aquatic insects typically consumed by swallows or phoebes. Prairie sunflowers were found to be the dominant food item of mourning doves in southeastern New Mexico [61].

Maximum Level: The highest DDE concentration was 4.9 mg/kg in a composite sample of 12 northern rough-winged swallows from both Castolon and Solis.

Predator Protection Level: The National Academy of Sciences has proposed a predator protection level of 1.0 mg/kg [17]. This level may not be low enough to protect peregrine falcons, since 1.0 mg/kg has more recently been reported as a dietary concentration that causes egg-shell thinning in peregrine falcons [12]. In Big Bend National Park, 1.0 mg/kg DDE was exceeded in four of five swallow and phoebe samples (Appendix 2).

DISCUSSION

Historically, the Big Bend area of Texas has produced relatively high concentrations of peregrines, presumably partly as a result of its near wilderness isolation from the modern world [13]. Prior to the advent of DDT/DDE and other modern toxic chemicals, peregrines in the Big Bend area were probably not exposed to elevated levels of synthetic chemicals.

Eggshell Thinning: Of the contaminants we found in the Rio Grande, DDE and its DDT relatives have been most strongly implicated in eggshell thinning in raptors [69]. Other contaminants found in notable quantities in Big Bend National Park, such as mercury, are not similarly correlated with eggshell thinning [69].

Aquatic Insects: The presence of DDE in aquatic insects in the Rio Grande at Big Bend National Park is of some concern, since aquatic insects provide one potential avenue for DDE to biomagnify up the avian food chain. Emerging aquatic insects are eaten by some species of small birds. Small insectivorous birds are eaten by peregrine falcons. Thus, our preliminary Big Bend National Park data leave open the possibility that aquatic insects may be a source of DDE being biomagnified into the peregrine falcon food chain. In this way, the Rio Grande may be serving as one potentially harmful source of DDE available to the peregrine falcons in Big Bend National Park. The idea that DDE may be biomagnifying from one Rio Grande trophic level to the next is supported by our data on aquatic insects and red shiners. The elevated concentrations of DDE we found in small birds such as swallows and phoebes also tend to indirectly support this concern (Appendix 2).

Small Birds: Peregrines eat small birds of all kinds, but the least safe birds for them to eat would be insectivorous and migratory birds rather than herbivorous and resident birds. This is because insectivorous and migratory birds would be suspected to have higher concentrations of DDE [12,13] .

Phoebes in the Big Bend area are considered to be primarily resident birds rather than migratory (Danny Swepston, Texas Parks and Wildlife, personal communication). Thus, the elevated DDE levels in Big Bend National Park phoebes may be especially significant, since levels this high in resident birds suggests the possibility that these resident birds are picking up the DDE in the Big Bend area. As summarized in the results section, preliminary indications are that levels of DDE in insectivorous birds in Big Bend are high enough to warrant concern for the peregrines that are consuming them.

Small Bird Migration: Resident birds and insects associated with the Rio Grande are not the only potential source of DDE to peregrines in Big Bend National Park, since prey-sized migratory birds in other parts of the western U.S. have also been found to have elevated DDE concentrations [7,60]. In the years 1976-1980, duck wing samples collected for the NCBP from the Rio Grande and Pecos River drainages of west Texas had the highest DDE levels in the nation [7,71]. Upstream of Big Bend National Park near Ruidosa, Presidio County, Texas, northern rough-winged swallows were collected that had whole-body DDE concentrations of 7.3 mg/kg (Charlie Sanchez, U.S. Fish and Wildlife Service, personal communication). This is even higher than the DDE levels we found in small birds in Big Bend National Park (Appendix 2).

The DDE concentrations in migratory prey-sized birds tends to be higher than concentrations in resident species, and those birds that migrate south of the U.S. tend to have elevated levels of DDE [12,60].

Peregrine Falcon Migration: Peregrines which migrate south of the U.S. border in the winter tend to pick up most of their DDE in Latin America [72]. Although some of the peregrines of Big Bend National Park tend to be relatively resident and apparently are not migrating farther south for the winter, others do move around some (Mike Fleming, National Park Service, personal communication). Thus, peregrines that leave Big Bend for periods of time may be picking up DDE elsewhere and even those peregrines that are year-round residents of Big Bend may be eating migratory birds that are bringing in body burdens of DDE from other parts of the U.S. or from foreign countries.

Potential Sources of DDT/DDE in the Rio Grande: Just as most clues point to Latin America as the source of DDE in migrating birds, most clues point to Mexico as the mostly likely source for DDE being brought into Big Bend National Park by the Rio Grande. Reasons for this preliminary assessment include the following: 1) The ban since 1972 on use and sale of DDT in the U.S., 2) the open sale of DDT on the streets of Juarez, Mexico, and its use in this Rio Grande city upstream of Big Bend [32], 3) DDE concentrations in sediments of the Rio Grande just below its confluence with the Rio Conchos were the highest recorded anywhere on the Rio Grande and were thought to be originating in Mexico (Jack Davis, Texas Water Commission, personal communication), 4) the Rio Grande above the Rio Conchos confluence is dry during many years, so the Rio Conchos is a logical source of contaminants in the Rio Grande at Big Bend National Park (Jim Scudday, Sul Ross University, personal communication), 5) reports of continued production of DDT in 1984 at a factory in Delicias, a Mexican town in the Rio Conchos drainage basin upstream of Big Bend [34], and 6) various reports of ease of purchasing DDT and continued use in Mexico and possibly a few border areas in the U.S. [32,33,34] .

Potential Sources of Other Contaminants in the Rio Grande: Due to unusually high Rio Grande flows for the last few years, there has sometimes been a more continuous flow in the river from El Paso to the Big Bend area [67]. A large amount of raw sewage, poorly treated sewage, and industrial wastes have been reported to be flowing into the Rio Grande

upstream of Big Bend National Park in the Anthony/El Paso/Juarez area [63,64]. Therefore, complex mixtures of contaminants may sometimes be transported by high flows to the Big Bend area.

Further suspicion that complex mixtures of contaminants may sometimes impact the Rio Grande in the Big Bend area as a result of sewage or industrial discharges is raised by a recent report submitted to our Regional Office of Endangered Species in Albuquerque [67]. This report documents that on February 23–29, 1988 (two years after our field work), the Rio Grande just below the confluence of the Rio Conchos differed from the Rio Grande upstream of the confluence in the following ways: 1) more black, anoxic silt (thought to be evidence of extreme sewage pollution) covering the bottom in areas of low stream velocity, 2) fewer numbers of fish species, 3) lower densities of the fish, 4) higher percentages of pollution–tolerant species, and 5) more foul smelling and scum covered backwater areas [67]. The highly degraded conditions were found only in the Rio Grande and not in tributaries or in the Rio Grande upstream of the Rio Conchos [67]. One conclusion of the 1988 fish survey report was that water quality and fish populations downstream of the Rio Conchos are apparently substantially degraded in comparison to their condition in 1977 [67].

RECOMMENDATIONS

Impacts of Mixtures of Toxic Chemicals: An issue deserving additional study is the potential problem of combined effects of elevated levels of several heavy metals and DDE on peregrine falcons and other predatory species of fish and wildlife. Information on the toxicity of combined body burdens of heavy metals and organic contaminants would be helpful in interpreting future studies nationwide as well as in Big Bend National Park. However, the complexity of such studies requires that they be done in research laboratories rather than in the field.

Definitive Studies: Since our field study was a preliminary survey, a more complete understanding of the extent to which contaminant problems in Big Bend National Park vary over time and during various flow and climatic regimes would require a more comprehensive follow–up field study.

We understand that additional studies related to water quality downstream of the Rio Conchos are underway at Sul Ross University. Following completion of these studies, the U.S. Fish and Wildlife Service will reassess future study needs.

Additional DDE Studies: The DDE aspects of the follow–up study might include determining which kinds of small birds in Big Bend are being preyed upon most by peregrines and which aquatic insects are being consumed by the small birds. A complete food habits study of peregrines in Big Bend National Park would be very helpful.

Since our DDE information is sparse, some of our information is several years old, and some of the suspected sources are based partly on information generated by newspaper reporters, new investigations by scientists or governmental officials would help determine their current validity. Future studies should use sufficient numbers of replicate samples of insects and birds to enable the investigators to do more definitive statistical analyses of the potential contaminant impacts than was possible in this initial survey. Peregrine eggshells that can be sampled without disturbing the falcons should also be analyzed for DDE and other organochlorine contaminants. Any dead peregrines found in the Big Bend area should be analyzed for DDE and other organochlorines after consultation with the Fish and Wildlife Service.

Eliminating DDE Sources: Although additional field contaminant studies would be generally instructive, we already know DDE is in Rio Grande fish and wildlife. Therefore, it would probably be more helpful to the peregrine falcons if a more intense effort was focused on finding and eliminating any remaining Mexican or U.S. sources of DDT/DDE entering the Rio Grande upstream of Big Bend before doing additional contaminants studies in the park itself. As in other locations, reproductive performance of peregrines may not improve until DDE levels in prey items is further reduced [12].

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Appendix 1

List of aquatic samples and residue values for selected contaminants.

Sample Number	ID Code[1]	Species Quantity)	Tissue Type	Moisture %	Lipids %	DDE (Mg/Kg)	Combined DDT (Mg/Kg)
1	CAS-SED-OR-Cl	Sediment (907 grams)	Fines	29.99	0.04	<0.007	<0.007
2	CAS-SED-OR-C2	Sediment (907 grams)	Replicate Fines	30.74	0.08	<0.003	<0.003
3	CAS-AQINS-OR	Aquatic Insect Larvae (73 grams)	Whole Body (Mostly Dragon fly Larvae and Helgrammites)	75.64	5.90	0.058	0.058
4	CAS-ADINS-OR	Adult Flying Insects (13 grams)	Whole Body Mostly Dragon flies)	68.78	3.63	<0.008	<0.008
5	CAS-CHC-Fillet-OR	Channel catfish (60 g., from one 560 mm long)	Fillet	80.15	3.60	0.12	0.126
6	CAS-CHC-WB-OR	Channel catfish (3,325-380 mm)	Whole Body	7.45	5.78	0.21	0.231
7	CAS-GAM-OR-Female	Gambusia affinis (44 at 115 grams)	Whole Body	79.51	3.83	0.16	0.185
8	CAS-GAM-OR-small	Gambusia affinis (50 at 24 grams)	Whole Body	83.49	3.22	0.081	0.094

[1] CAS = Castolon, SOL = Solis, CR = Organics, MET = metals, Cl - replicate # 1

Appendix 1, continued.

Sample Number	ID Code[1]	Species (Quantity)	Tissue Type	Moisture %	Lipids %	DDE (Mg/Kg)	Combined DDT (Mg/Kg)
9	CAS-TSS-Biggest 5-OR	Texas spiny soft shell turtle (5 at 230-270 mm)	Whole Body	79.13	1.27	0.53	0.543
10	CAS-TSS-Smallest 5 5-OR	Texas spiny soft shell turtle (5 at 135 to 140 mm)	Whole Body	77.79	1.61	0.18	0.195
11	CAS-RCS-OR	River carp sucker 3 (312 to 390 mm)	Whole Body	69.04	11.30	0.52	0.562
12	CAS-LNG-LIVER/FAT-OR	Longnose gar (100 grams from one 1055 mm long)	Liver, Ovaries Fatty tissue	67.39	18.82	7.9	8.67
13	CAS-NL-OR	Notropis lutrensis (40 at 63 grams)	Whole Body	77.84	6.55	0.27	0.295
14	CAS-LNG-WB-OR	Longnose gar (1 at 562 mm)	Whole Body	64.84	6.91	1.75	1.903
15	CAS-GS-WB-OR	Gizzard shad (3 at 318 to 350 mm)	Whole Body	75.26	4.07	0.48	0.549

Appendix 1, continued.

Sample Number	ID Code[1]	Species (Quantity)	Tissue Type	Moisture %	Lipids %	DDE (Mg/Kg)	Combined DDT (Mg/Kg)
16	SOL-SED-OR-C1	Sediment (454 grams)	Sediment Fines	51.57	11.30	0.60	0.625
17	SOL-SED-OR-C2	Sediment (454 grams)	Sediment Fines (Replicate)	55.31	0.05	<0.003	<0.003
18	SOL-GAM-OR-Female	Gambusia affinis (21 at 36 grams)	Whole Body	79.9	2.54	0.170	0.186
19	SOL-GAM-OR-Small	Gambusia affinis (69 at 17 grams)	Whole Body	81.76	2.66	0.51	0.51
20	SOL-LNG-Eggs-OR	Longnose gar (60 grams)	Eggs from Gravid Female (790 mm long)	73.62	6.49	1.90	2.148
21	SOL-NL-OR	Notropis lutrensis (12 at 21 grams)	Whole Body	76.69	2.33	0.160	0.175
22	SOL-AQINS-OR	Aquatic insect larvae (15 grams)	Whole Body - (Mostly Dragonfly larvae and water bugs)	77.18	1.84	0.12	0.139

Appendix 1, continued.

Sample Number	ID Code[1]	Species (Quantity)	Tissue Type	Moisture %	Lipids %	DDE (Mg/Kg)	Combined DDT (Mg/Kg)
23	SOL-LNG-LIVER-OR	Longnose gar (16 grams)	Liver Tissue from 4, 490-790 mm long	74.44	3.17	0.61	0.61
24	SOL-CHC-Fillet-Cl-Largest 4-OR	Channel catfish (4)	Fillets frm Largest 4 (440-610 mm)	82.29	1.15	0.069	0.086
25	SOL-CHC-WB-OR-C4	Channel catfish (2)	Whole Body (smallest 2, 120-230 mm)	79.49	2.78	0.22	0.239
26	SOL-CHC-Fillet-OR-C3	Channel catfish (4)	Fillets frm Intermediate 4 (290-420 mm)	82.22	1.17	0.037	0.042
27	SOL-CHC-Liver-Cl-(largest 4)-OR	Channel catfish (4)	Liver from largest 4 (440-610 mm)	75.86	9.88	0.43	0.57

Appendix 1, continued.

Sample Numbe	ID Code[1]	Species (Quantity)	Tissue Type	Moisture %	Selenium (Mg/Kg)	Chromium (Mg/Kg)	Mercury (Mg/Kg)	Vanadium (Mg/Kg)
28	CAS-SED-MET-Cl	Sediments (227 grams)	Sediment Fines	NA	1.6	8.8	<0.19	24.0
29	CAS-SED-MET-C2	Sediments (227 grams)	Sediment Fines (Replicate)	NA	1.2	7.4	<0.18	24.0
30	CAS-AQINS-MET	Aquatic Insect Larvae (29 grams)	Whole Body composite of Dragonfly larvae and helgrammites	77.50	0.54	2.4	<0.045	<0.098
31	CAS-CHC-Fillet-MET	Channel catfish (1 at 560 mm)	Fillet (60 grams)	80.09	0.25	0.13	0.073	<0.097
32	CAS-GAM-MET-FEMALE	Gambusia affinis , (10 at 30 grams)	Whole Body	77.11	0.45	0.14	0.062	0.11
33	CAS-GAM-MET-Mixed	Gambusia affinis, (20 at 21 grams)	Whole Body - both male and female	80.58	0.45	0.18	<0.05	0.14
34	CAS-NL-MET	Notropis lutrensis (20 at 38 grams)	Whole Body (35-62 mm)	76.08	0.95	0.22	0.053	0.22

Appendix 1, continued.

Sample Number	ID Code[1]	Species (Quantity)	Tissue Type	Moisture %	Selenium (Mg/Kg)	Chromium (Mg/Kg)	Mercury (Mg/Kg)	Vanadium (Mg/Kg)
35	CAS-TSS-Intermediate-MET	Texas spiny soft shell turtle (5 at 170-230 mm)	Whole Body	77.27	0.64	0.96	0.073	0.20
36	CAS-LNG-MET-REST	Longnose gar (1 at 1055 mm)	Rest of Body (Missing Fatty Internal Organs)	56.76	0.40	0.91	0.82	0.13
37	CAS-GS-WB-MET	Gizzard shad (2, 310-313 mm)	Whole Body	78.35	1.1	<0. 10	<0.05	0.90
38	SOL-SED-MET-Cl	Sediment (227 grams)	Sediment Fines	NA	1 .8	8. 6	<0.17	26.0
39	SOL-SED-MET-C2	Sediment (227 grams)	Sediment Fines (Replicate)	NA	0.61	7. 2	<0.16	26.0
40	SOL-GAM-MET-Female	Gambusia affinis, (30 at 43 grams)	Whole Body	77.22	0.65	0.54	0.065	0.22
41	SOL-CHC-Fillet-C1-Largest-MET	Channel catfish (largest 4, 440-610 mm)	Fillet Composite	81.00	0.52	0.88	0.18	<0.96

Appendix 1, continued.

Sample Number	ID Code[1]	Species (Quantity)	Tissue Type	Moisture %	Selenium (Mg/Kg)	Chromium (Mg/Kg)	Mercury (Mg/Kg)	Vanadium (Mg/Kg)
42	SOL-CHC-Fillet-MET-C3	Channel catfish (Intermediate 4, 290-420 mm)	Whole Body	81.51	0.42	0.33	0.062	<0.097
43	SOL-CHC-WB-MET-C2	Channel catfish (Small 2, 190-280 mm)	Whole Body	79.56	0.38	<0.097	0.068	0.13
44	SOL-LNG-Liver-MET	Longnose gar (4, 445-790 mm)	Liver Composite	76.03	3.6	0.46	8.7	1.4
45	SOL-LNG-Rest-MET	Longnose gar (same 4)	Whole Body minus liver	69.29	0.058	0.22	0.70	0.17

Appendix 2

List of bird samples and whole-body residue values for selected contaminants.

Sample Number	ID Code	Species (Quantity)	Location(s)	Moisture %	Lipids %	DDE (Mg/Kg)	Combined DDT (Mg/Kg)	beta-BHC
46	PP-4	Northern rough-winged swallow (12)	Castolon and Solis	66.6	9.28	4.9	4.9	0.05
47	PP-5	Mourning dove (7)	Castolon and Solis	64.8	7.81	0.01	0.01	0.01
48	PP-6	Cliff swallow (4)	Castolon and Solis	68.9	11.4	2.1	2.1	0.02
49	PP-7	Black phoebe (3)	Castolon and Solis	75.3	3.61	1.2	1.2	0.02
50	PP-11	White-winged dove (6)	Castolon and Solis	68.6	5.51	0.02	0.02	<0.01
51	PP-12	Black phoebe (4)	Castolon	71.6	3.53	1.7	1.7	0.01
52	PP-13	Black phoebe (5)	Solis	71.7	4.0	0.55	0.55	<0.01
53	PP-14	Mourning dove	Solis	66.6	6.97	<0.01	<0.01	<0.01